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BELLCOMM, INC.
955 L'ENFANT PLAZA NORTH, S.W. WASHINGTON, D.C. 20024

SUBJECT: Description of Molecular Sieve CO_2 Removal System - Case 620

DATE: December 20, 1968

FROM: J. J. Sakolosky

ABSTRACT

A molecular sieve is a regenerable system that removes CO_2 from the spacecraft cabin atmosphere. This function is accomplished by an adsorption process which depends on the physical properties of the CO_2 molecule and the molecular sieve adsorbing material. The sieve is regenerated (that is, CO_2 molecules are desorbed from the molecular sieve) by the application of heat or a decrease in bed pressure or a combination of the two. Molecular sieve material has a higher affinity for water than for CO_2; thus, the atmosphere must be predried before entering the CO_2 removal bed.

Two-bed systems and four-bed systems are in common use. The difference between a two-bed system and a four-bed system is that, in the latter, the predrying material is not in the same canister as the CO_2 removal bed, and thus can be desorbed separately to conserve water. Other aspects of these two configurations are discussed.

The Air Research molecular sieve for AAP-2 is a two-bed system that is desorbed to space vacuum. A number of redundant features are incorporated in the design to protect against system failures. Design parameters for the Air Research molecular sieve and a system schematic diagram are discussed.

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MEMORANDUM FOR FILE

INTRODUCTION

Lithium Hydroxide (LiOH) has been used to remove CO_2 from the cabin atmosphere in all U. S. manned space flights. However, for long duration missions (greater than several weeks), the weight penalty associated with LiOH is excessive, and it becomes advantageous to use a regenerable system for CO_2 removal.

A regenerable system that has evolved during approximately ten years of research and development is the molecular sieve. The CO_2 removal mechanism of the molecular sieve is well understood and has been verified during thousands of hours of laboratory and development tests -- both manned and unmanned. The first operational uses of molecular sieves in the U. S. manned space program will be in the Apollo Applications Program and the Air Force MOL program.

MOLECULAR SIEVE MATERIAL

The heart of the CO_2 removal system is the molecular sieve material used for adsorbing CO_2. It is synthetic zeolite (chemically an alumino-silicate) often referred to by the manufacturers name followed by a type number (e.g. Linde Type 13X). The material has a crystalline structure which is extremely porous. Pore size and shape are controlled to selectively adsorb or reject particular gas molecules. As a result of its extreme porosity, the specific surface area available for adsorption runs as high as 700-800 m^2/gm. The material is relatively inert so that the danger of reaction (and consequent degradation of the CO_2 adsorption capacity) with contaminants within the cabin atmosphere is small. Molecular sieve material is usually produced in the form of small pellets or granules. These exhibit high strength characteristics which sustain the material through the extreme vibrational and acceleration environment at launch. The major disadvantage of the material is its extreme sensitivity to water; that is, it will preferentially adsorb water over CO_2 molecules. This necessitates removal of water from the cabin atmosphere before it enters the molecular sieve CO_2 removal material. Water is removed in a predrying bed which, depending on the particular system configuration, may be either silica gel or molecular sieve material itself.

MOLECULAR SIEVE ADSORPTION PROCESS

The CO_2 adsorption procedure characteristic of all molecular sieves is shown in block diagram form in Figure 1. After passing through a condensing heat exchanger for partial water removal, the cabin air stream is directed through a predrying bed where it is dried to a dew point of approximately -50°F. The extremely dry air exiting the predrier is then passed through the CO_2 removal bed. "Clean" air from the bed is directed back to the cabin atmosphere. A second system identical to that shown in Figure 1 would simultaneously be desorbing water and CO_2 previously accumulated. The two parallel systems are periodically cycled to provide a continuous CO_2 removal capability.

The mechanism by which CO_2 is removed from the air is an "adsorption" rather than an "absorption" process. (The reaction of CO_2 with LiOH is an "absorption" process.) The interaction between the adsorbed molecule and the adsorbing material is the result of a physical attraction; no chemical reaction takes place. There is general agreement that the attractive force is electrical and takes place on the molecular level. It is highly dependent on the atomic structure of the adsorbate and adsorbent molecules.

During the system operation, gas molecules are simultaneously adsorbing and desorbing from the surface of the molecular sieve material. Adsorption and desorption can be thought of as competing processes in which the number of adsorbing molecules and the number of molecules leaving the surface are striving to reach an equilibrium point at which the net adsorption (or desorption) rate is zero. This equilibrium point determines the adsorption capacity of the bed and is dependent on a number of factors -- the two most important being bed temperature and CO_2 partial pressure. The direction of the process (that is, adsorption or desorption) can be controlled by varying these parameters. Figure 2 indicates that bed adsorption capacity decreases with decreasing CO_2 partial pressure and with increasing bed temperature. Thus a saturated bed may be regenerated by subjecting it to a low external pressure or by increasing its temperature.

Upon adsorption, the energy state of the adsorbed molecule is decreased; this release of energy manifests itself in the form of heat. Therefore, during adsorption the temperature of the molecular sieve bed increases unless a means of removing the heat of adsorption is provided. This heat released during adsorption becomes an important factor in system design since, as we have already seen, bed adsorption capacity is highly dependent on temperature.

A mass transfer zone concept is often used in system design; Figure 3 illustrates this approach. Adsorption takes place within the boundaries of the mass transfer zone. This adsorption zone travels along the length of the bed in the direction of air flow (from left to right in the Figure). The slope of the curve within the mass transfer zone is an indication of the rate at which adsorption is taking place; for example, a horizontal line (zero slope) corresponds to a zero net adsorption rate whereas a very steep slope would indicate that adsorption is occurring rapidly.

When the front of the mass transfer zone reaches the end of the bed, CO_2 will appear in the effluent gas stream. It is at this point that one would like to initiate the desorption cycle for the bed. If the mass transfer zone is long, a large portion of the bed will remain unsaturated. This means inefficient bed utilization, and the unsaturated portion of the bed constitutes an undesirable weight penalty. Clearly, maximum utilization of available bed capacity will be obtained if the mass transfer zone is kept as short as possible. Keeping the mass transfer zone short is a difficult design task since zone length depends on a number of factors such as flow velocity, CO_2 partial pressure, adsorbent pellet size, bed and gas stream temperatures, total pressure, and residual concentration of CO_2 within the sieve.

DESORPTION PROCEDURES

Regeneration of saturated molecular sieve material is accomplished by changing the equilibrium adsorption capacity of the bed. This may be accomplished by either increasing bed temperature or by decreasing CO_2 partial pressure.

The simplest of the desorption procedures consists of venting the saturated bed to space vacuum; this is known as the pressure-swing technique. The low pressure surrounding the bed results in a net desorption of CO_2 (or water) molecules until a new equilibrium point is reached. Bed adsorption capacity may also be decreased through the addition of heat. Thermal-swing desorption makes use of this fact and drives molecules from a saturated bed by increasing its temperature. A third desorption technique in common use is purge gas stripping. This consists of purging the bed with a heated gas during the desorption cycle. The sweeping action of the gas in combination with the heat transfer acts to desorb the bed more efficiently than the relatively slow gas diffusion which takes place in the pressure-swing and thermal-swing techniques. Purge gas stripping is often used when desorption takes place to the higher pressures of the cabin atmosphere. In practice, two or more of the desorption procedures described above are often combined in a single system.

MOLECULAR SIEVE SYSTEM CONFIGURATIONS

The molecular sieve systems in common use are referred to in the literature as a two-bed system and a four-bed system (see Figure 4 and Figure 6). This nomenclature is misleading and often serves as a source of confusion to those not already familiar with molecular sieve design. A more accurate description would be a two-canister system or a four-canister system. Both contain four beds -- two for predrying and two for CO_2 removal. The difference between the two systems is that the first (two-bed) contains both the water and CO_2 adsorption beds within a single canister whereas the second (four-bed) has each bed in a separate canister.

Because the two-bed system contains both water and CO_2 sorbents within the same canister, desorption of CO_2 to space vacuum also requires the dumping of water. Therefore the two-bed system is commonly used when water recovery is not necessary. When only pressure-swing desorption is used, this system is called "two-bed adiabatic." The two-bed adiabatic configuration is shown in Figure 4. If thermal-swing desorption is combined with pressure-swing desorption to space vacuum, the system is called "two-bed thermal-swing." This configuration is shown in Figure 5.

The primary advantage of the two-bed adiabatic configuration of Figure 4 is its simplicity. After passing through a condensing heat exchanger, the air stream enters the system and is valved through the adsorbing canister and then back to the cabin. The second canister is simultaneously desorbing H_2O and CO_2 to space vacuum. In this configuration, molecular sieve material is often used for the H_2O bed as well as the CO_2 adsorption bed since it desorbs easily to space vacuum and actually has a higher affinity for water than silica gel. The primary disadvantage of this system is its heavy weight. Because of the heating effects associated with adsorption, large size beds must be utilized to make up for the corresponding decrease in adsorption capacity.

The two-bed thermal-swing configuration is very similar to that of the two-bed adiabatic; the only change is an added interface with an active thermal control system. Active thermal control improves overall system efficiency by maintaining a constant bed temperature during adsorption ($\sim 60^{\circ}F$) and desorption ($\sim 100^{\circ}F$). This increased efficiency leads to smaller bed sizes and consequently lower system weight. The major disadvantage of thermal swing is the increased complexity of the added thermal interface.

The four-bed system is shown in Figure 6. Each of the four beds are contained in separate canisters, which permits the conservation of water or CO_2 or both. The four-bed system is significantly more complex than the two-bed configuration because of the complex control associated with the valve and ducting network. For long duration missions, however, the additional system weight and complexity are more than compensated for by the water and CO_2 conservation capability.

In the four-bed configuration, air enters the system from a condensing heat exchanger and then is further dried to a $-50^{\circ}F$ dewpoint by the predrying bed. After passing through the CO_2 adsorption bed, the "clean," dry air is directed through the desorbing water bed. The dry air stream picks up water from the desorbing bed and returns it to the cabin atmosphere where it can be recovered by the condensing heat exchangers. The desorbing CO_2 bed may be vented to space vacuum or returned to a CO_2 accumulator. Note that in this particular configuration all three standard desorption techniques -- pressure-swing, thermal-swing, and purge gas stripping -- are combined.

In the four-bed configuration, the predrying bed is usually composed of silica gel. Silica gel has very little affinity for CO_2, an important characteristic since the water bed is desorbed to the cabin atmosphere. Silica gel is also easier to desorb at the higher total pressure of the cabin atmosphere.

Although not shown in Figures 4, 5, and 6, each of the configurations described above have electrical heating coils imbedded in the CO_2 adsorbent beds. During normal operation, the CO_2 adsorbent beds become slowly contaminated with water as a result of the imperfect drying of the atmosphere prior to entering the CO_2 bed. This progressive water contamination slowly reduces the CO_2 adsorption capacity of the bed so that periodic bake-out is required. Bake-out consists of heating the bed to a high temperature ($\sim 400^{\circ}F$) and desorbing to space vacuum for 5 to 10 hours until the residual contaminant concentration within the bed is approximately zero. Bake-out capability also provides a safeguard against water contamination resulting from a failure in the condensing heat exchanger.

A weight comparison of the three molecular sieve configurations is shown in Figure 7. The important point to note here is the relative weight of the three configurations; in practice, any particular design may vary considerably from the weights of Figure 7. The weights shown are somewhat heavier than often seen in the literature, and correspond to designs with a high level of built in redundancy. The systems are each sized for a three-man crew. The weight shown for the two-bed adiabatic system corresponds to the Air Research design for AAP-2. The slope of each curve results from the weight penalty attributed to the atmospheric loss during desorption. A dashed line is also shown indicating the equivalent weight of a two-bed adiabatic system when penalized for water lost overboard. The water penalty was assumed to be 5 lbs/day, the projected figure for the AAP-2 molecular sieve.

AAP-2 MOLECULAR SIEVE

The Airlock Module molecular sieve is a two-bed, adiabatic system designed by the Air Research division of the Garrett Corporation. Various design features of the system are shown in Figure 8. A schematic which indicates interfaces with other spacecraft systems is shown in Figure 9.

Air flow into the system divides between a charcoal odor adsorption canister, a bypass line, and the adsorbing molecular sieve canister. The desorbing bed is vented to space vacuum through a three inch duct. The gas selector valves used to control canister cycling are pneumatically controlled by the use of high pressure (100 to 250 psi) oxygen. An automatic cycle timer is used to control solenoid actuation valves in the oxygen pressurization sequence. Electrical heaters imbedded in each canister provide a bake-out provision in the event the beds become contaminated with water.

As can be seen from Figure 9, a large amount of redundancy has been incorporated in the molecular sieve design. Redundant automatic cycle timers are used to control the solenoid actuation valves; the temperature controllers for the bake-out heaters are also redundant. Manual interconnect valves add a level of redundancy in the oxygen pressurization network so that up to two solenoid valves may fail without affecting automatic actuation of the gas selector valves. The solenoid valves and gas selector valves may be actuated either automatically or manually. Finally, if one adsorbent canister becomes irreversibly disabled, emergency operation utilizing only one canister is possible. One canister operation will maintain the cluster CO_2 level at 15 mmHg as opposed to the normal maximum level of 7.6 mmHg during two canister operation. A CO_2 level of 15 mmHg is considered an emergency limit in the AAP program. The length of time for which this level is acceptable depends to a large degree on whether the crew is experiencing any discomfort.

J. J. Sakolosky

1022-JJS-ms J. J. Sakolosky

Attachments
Figures 1-9

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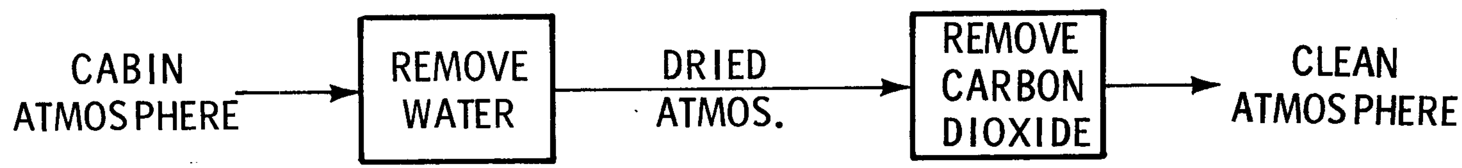

FIGURE 1 - MOLECULAR SIEVE ADSORPTION PROCESS

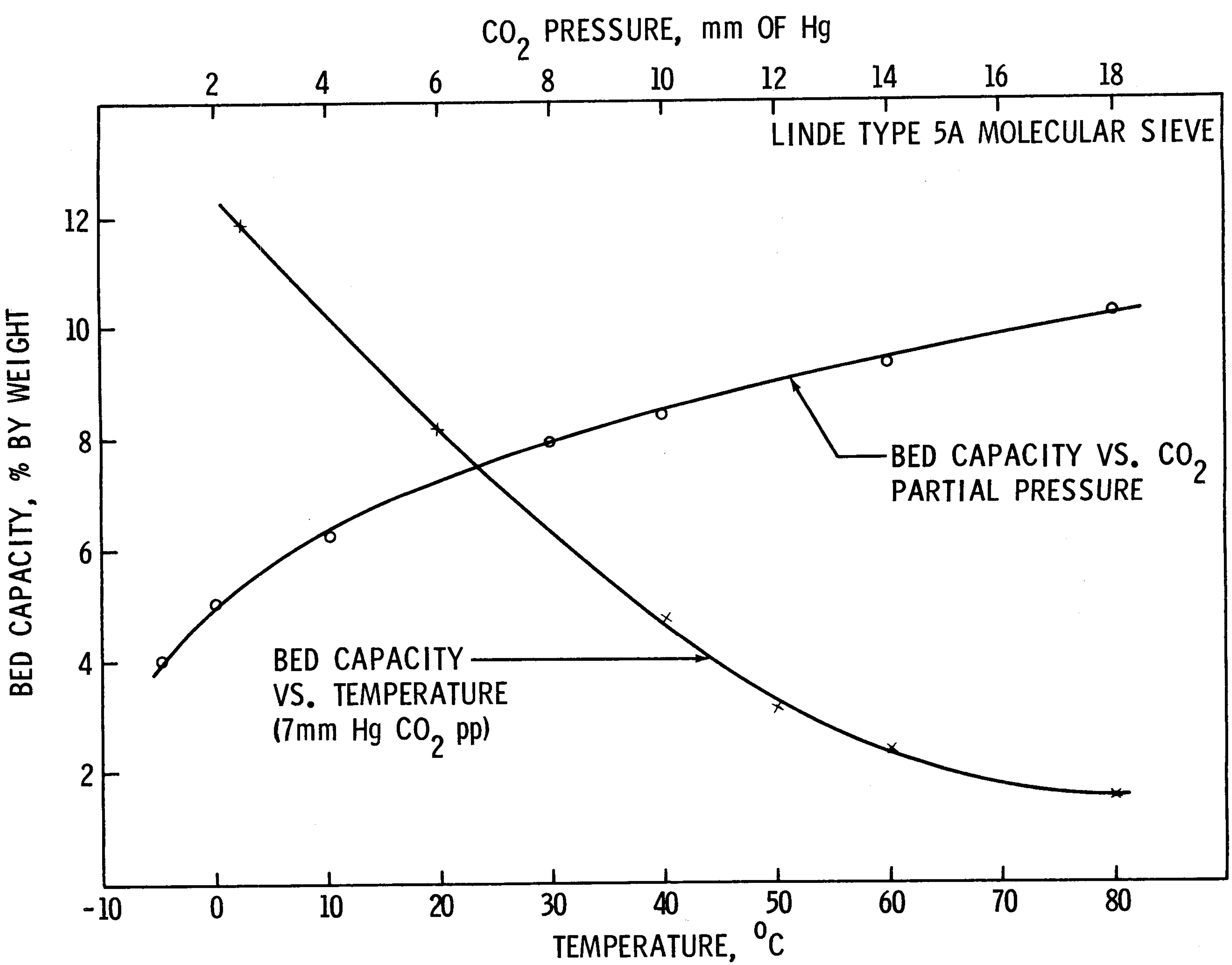

FIGURE 2 - MOLECULAR SIEVE BED CAPACITY AS A FUNCTION OF BED TEMPERATURE AND CO_2 PARTIAL PRESSURE

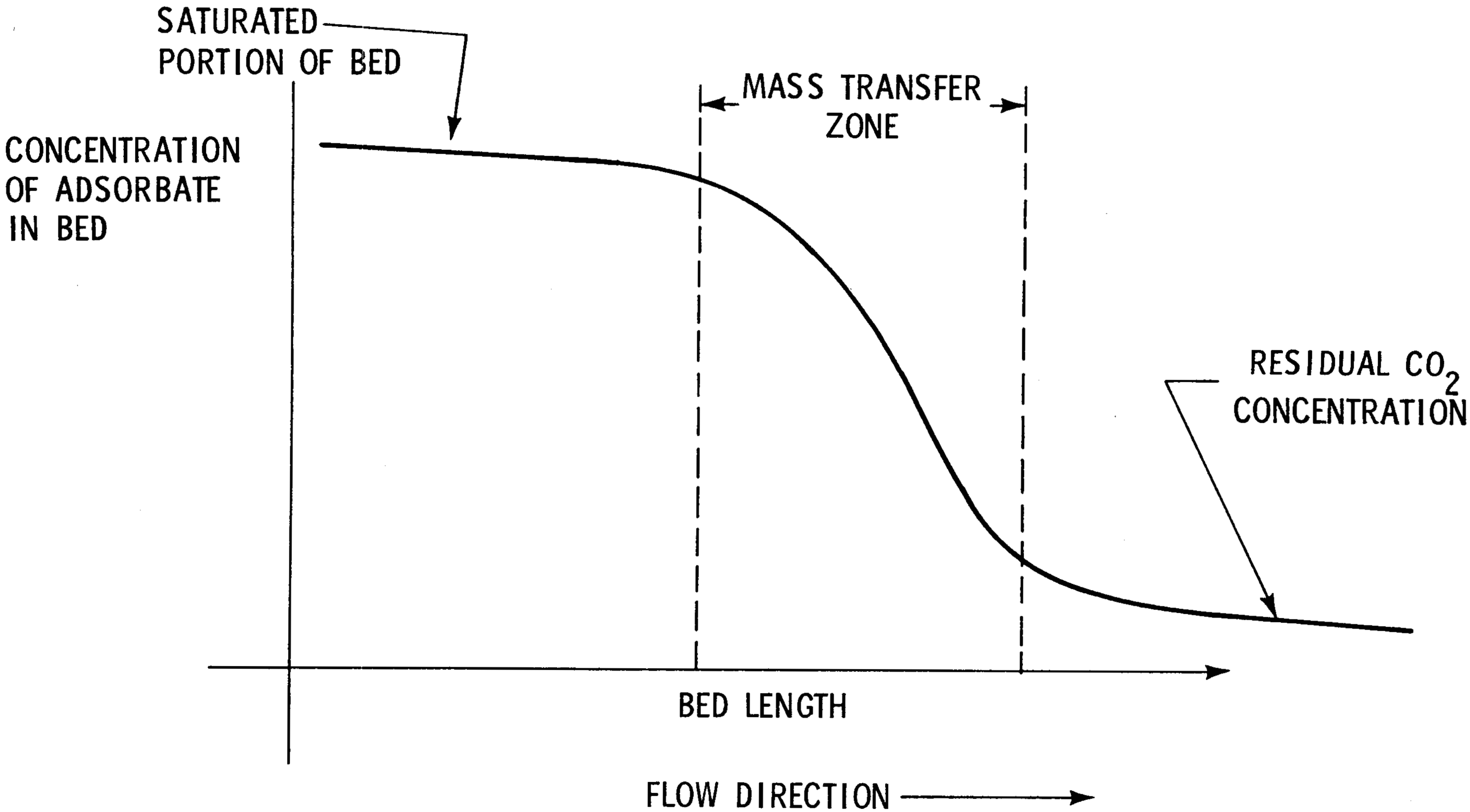

FIGURE 3 - CO_2 ADSORPTION PROFILE THROUGH BED CANISTER

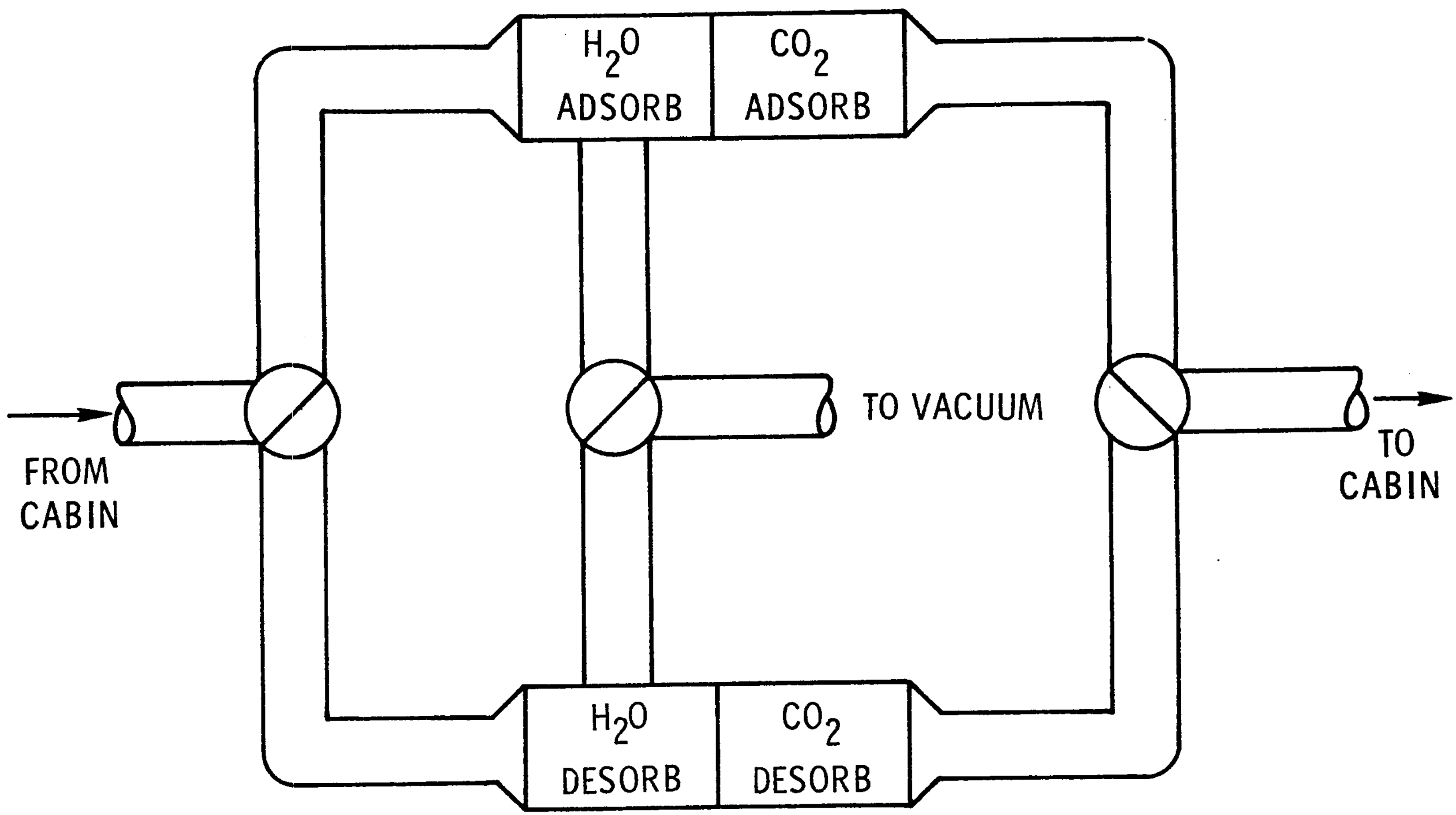

FIGURE 4 - TWO BED ADIABATIC MOLECULAR SIEVE CONFIGURATION

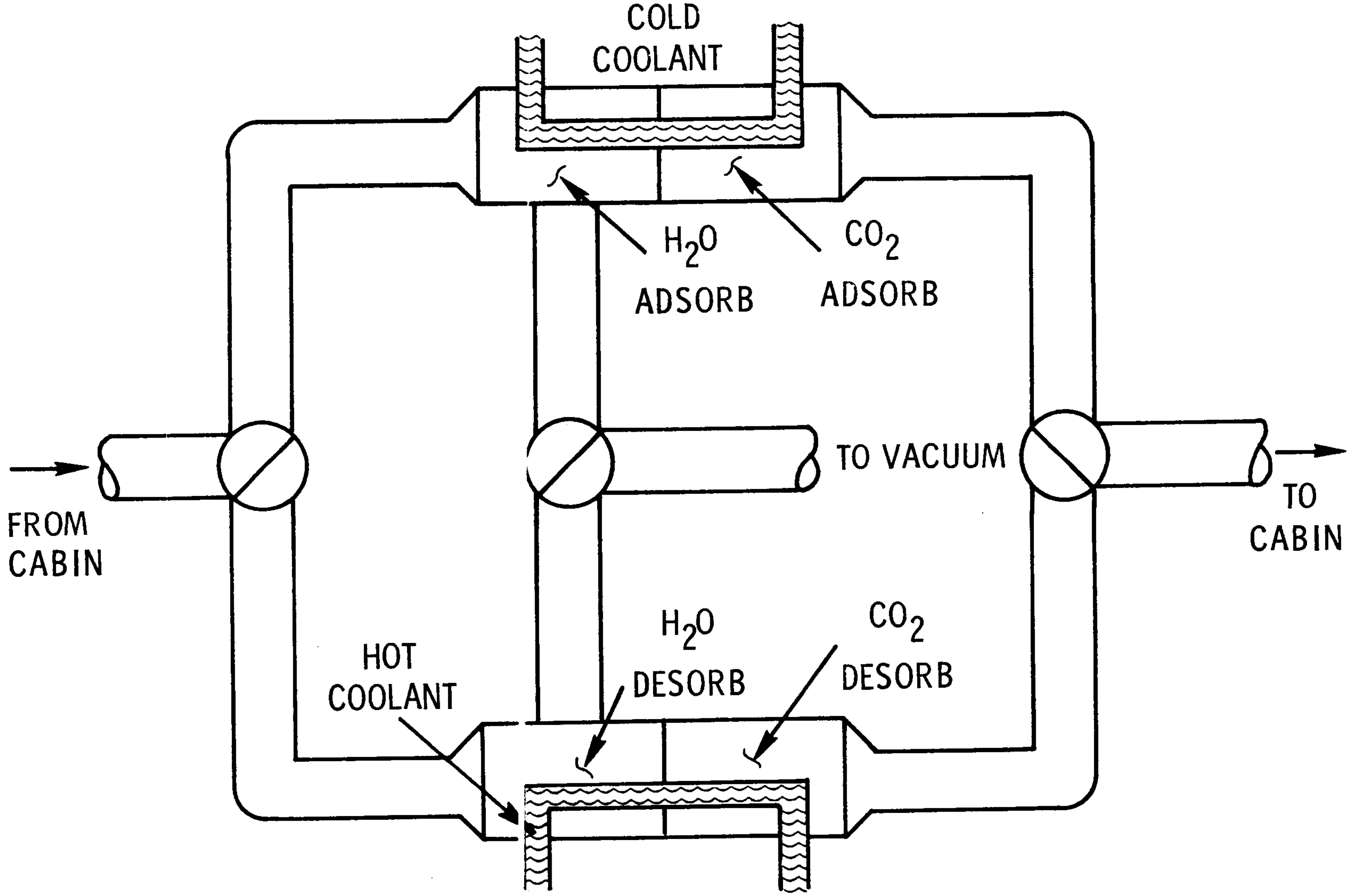

FIGURE 5 - TWO BED THERMAL SWING MOLECULAR SIEVE CONFIGURATION

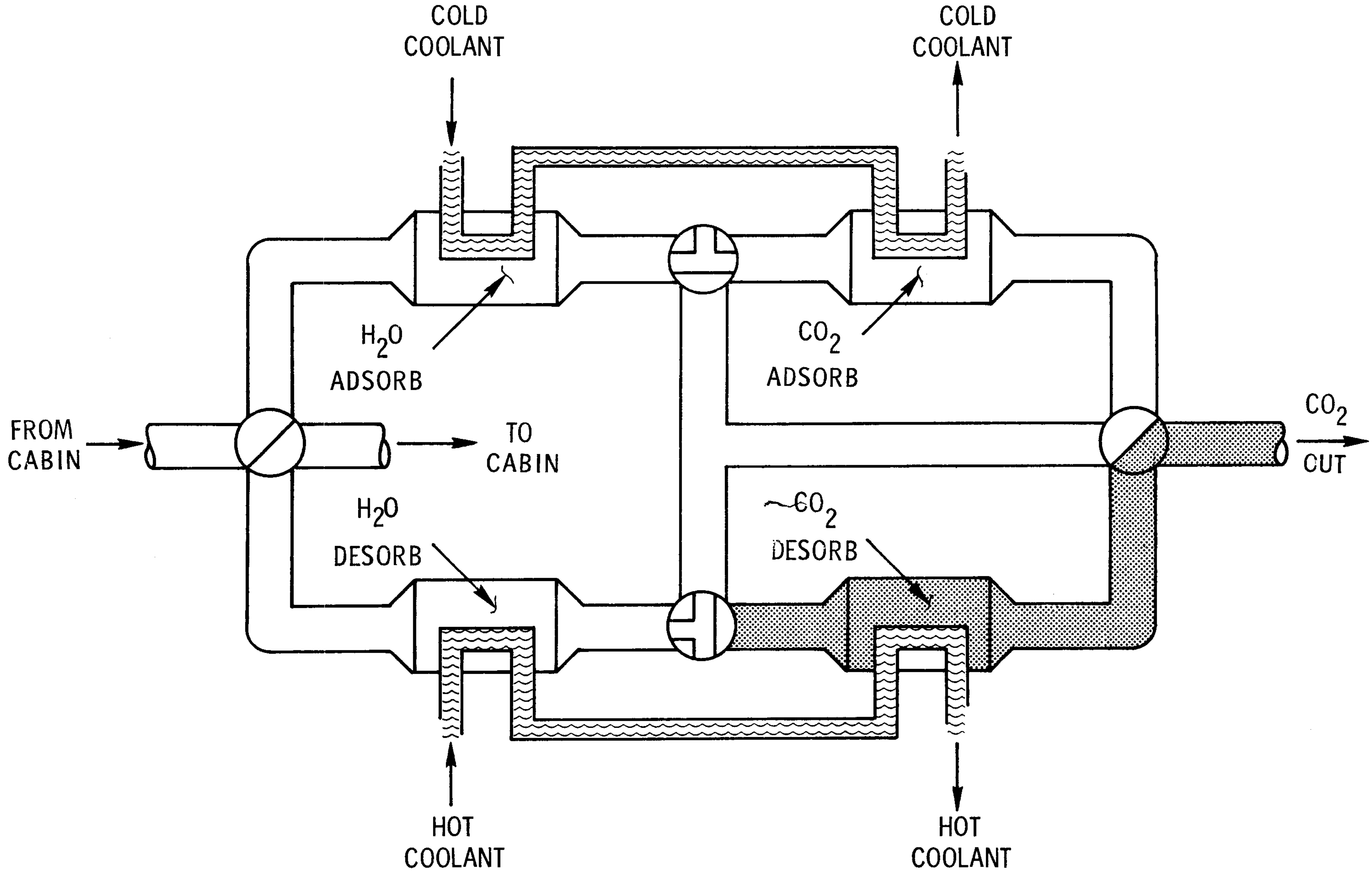

FIGURE 6 - FOUR BED THERMAL SWING MOLECULAR SIEVE CONFIGURATION

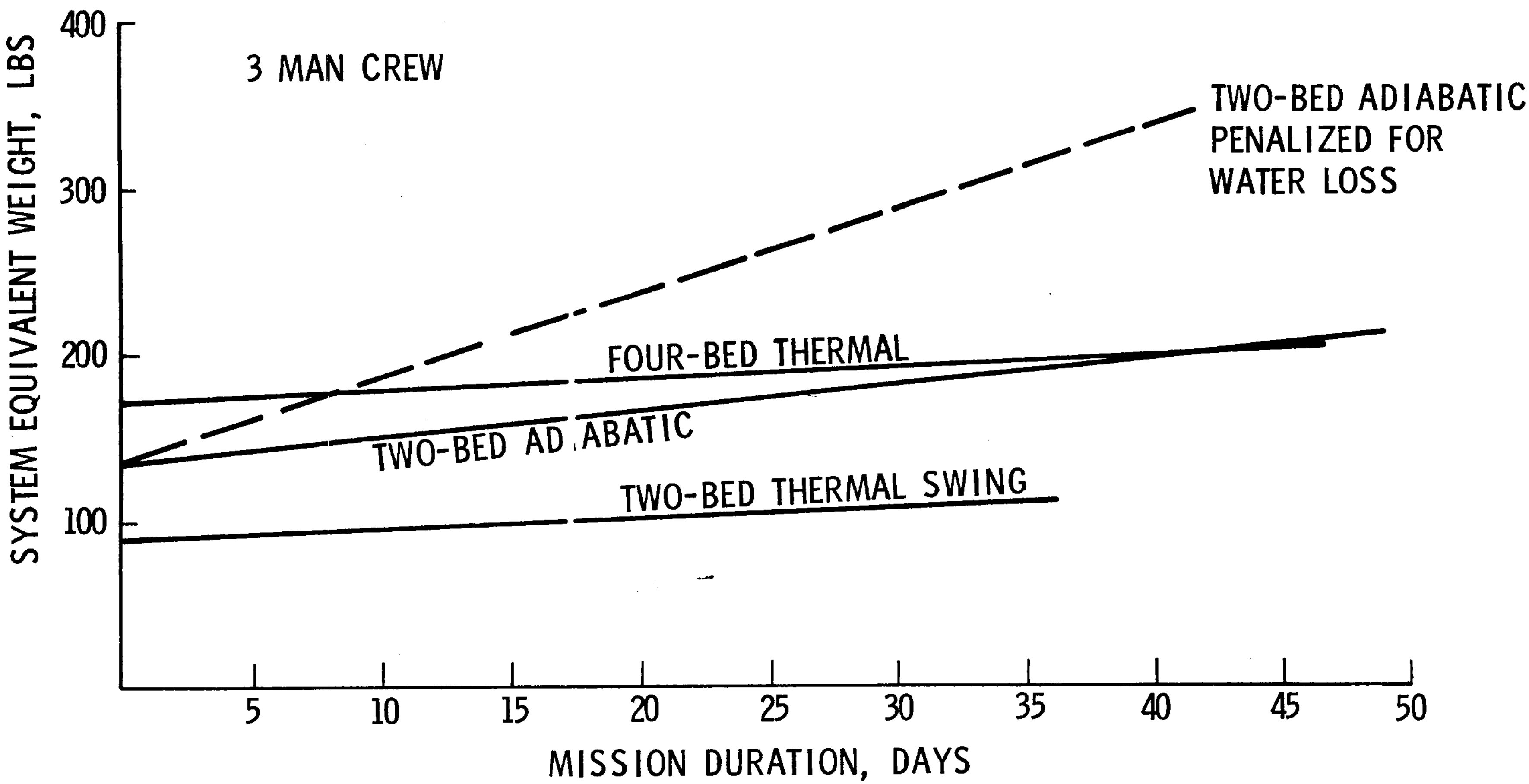

FIGURE 7 - WEIGHT COMPARISON OF BASIC MOLECULAR SIEVE CONFIGURATIONS

- WEIGHT - 135 LBS
- POWER - 3.8 W NOMINAL, 360 W BAKEOUT
- CYCLE TIME - 30 MINUTES
- CO_2 REMOVAL - LINDE TYPE 5A - 6.75 LBS/DAY
- H_2O REMOVAL - LINDE TYPE 13X - 5.1 LBS/DAY
- CABIN ATMOS. LOSS - 1.5 LBS/DAY
- CO_2 PARTIAL PRESSURE - 7.6 MM Hg

FIGURE 8 - AAP-2 MOLECULAR SIEVE DESIGN FEATURES

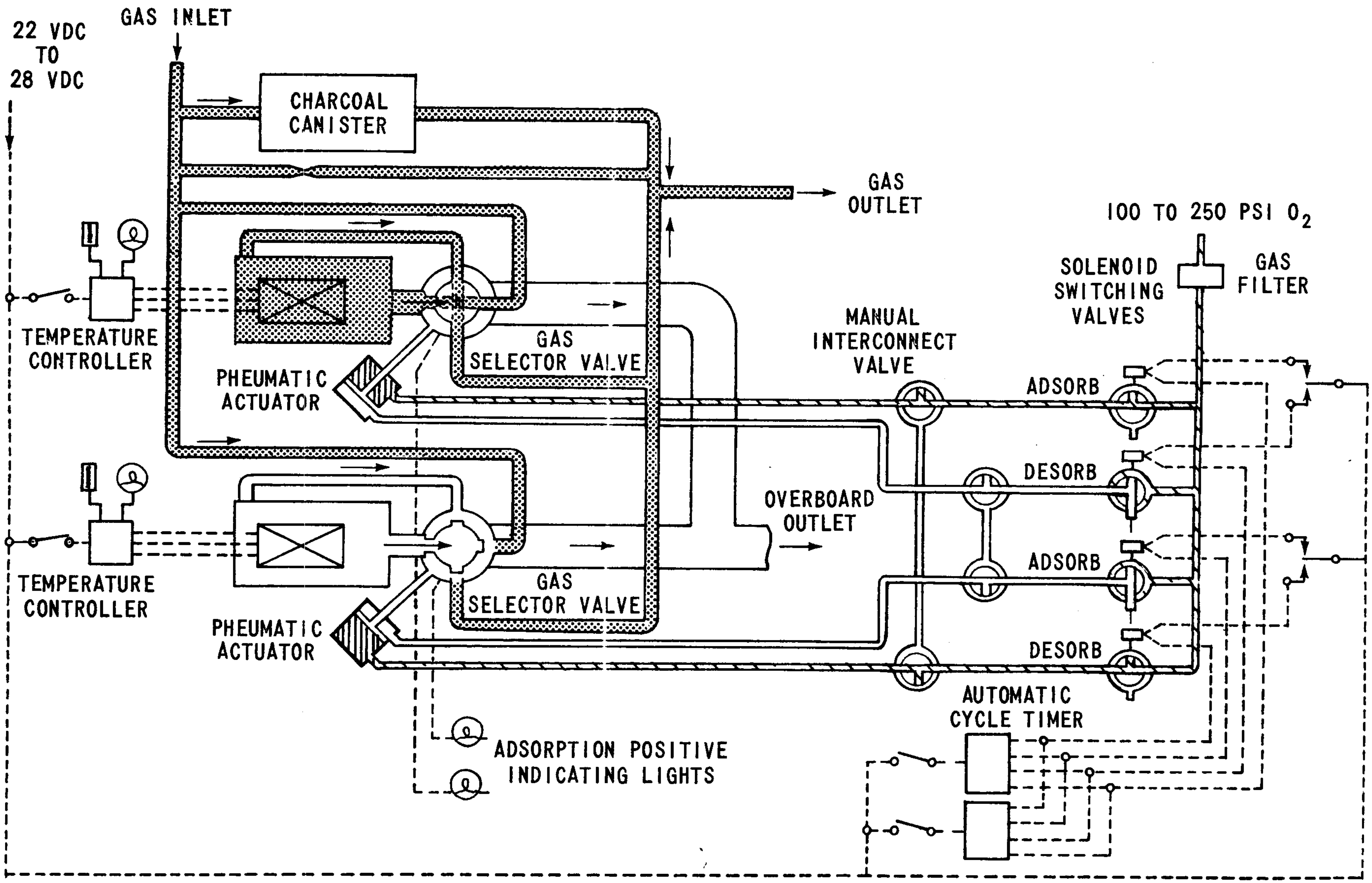

FIGURE 9 - AIR RESEARCH MOLECULAR SIEVE SCHEMATIC